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INTERNAL CATALYST BREAKUP PHENOMENA

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United Technologies Research Center

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INTERNAL CATALYST BREAKUP PHENOMENA

FINAL REPORT

UNITED TECHNOLOGIES RESEARCH CENTER
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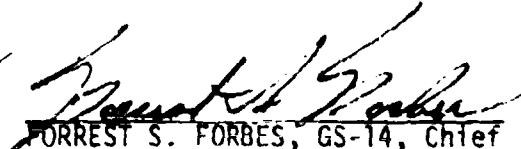
FOREWORD

This report was submitted by United Technologies Research Center, East Hartford CT 06108, under Contract F04611-74-C-0034, Job Order Number 305811PM with the Air Force Rocket Propulsion Laboratory, Edwards AFB CA 93523.

This report has been reviewed by the Information Office/DOZ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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Experimental studies were conducted to investigate catalyst particle breakup caused by internal stresses generated by pressure and temperature gradients typical of the operating environment of a hydrazine catalytic reactor. In previous studies, breakup caused by large pressure gradients had been illustrated under conditions in which liquid hydrazine wetting the outside surface of catalyst particles blocked the escape of gaseous decomposition products. In the experiments reported here, individual particles were

subjected to wetting and subsequent internal pressure buildup in a liquid
flow reactor. Breakup following liquid immersion was found to be most
frequent at low hydrazine temperatures and for catalyst particles of low
activity. Breakup is also affected by the physical characteristics of
catalyst particles; particle heating and hydrogen preconditioning can,
under certain conditions, lead to reduction in breakup without change in
catalyst activity. This implies changes in pore size distribution,
surface wettability or particle strength characteristics.

Individual particles were subjected to a series of screening tests
to evaluate the effects on breakup of thermal stress and fatigue. Thermal
shock and thermal cycling produced breakup only under the most severe
cooling conditions.

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SUMMARY

This report presents the results of a program conducted at United
Technologies Research Center under Contract F04611-74-C-0031 for the Air Force
Rocket Propulsion Laboratories. An important relationship between catalyst
reactivity in hydrazine and catalyst wetting and subsequent breakup has been
uncovered in this experimental program. In previous studies, wetting by
liquid hydrazine had been shown to lead to gas pressure buildup in catalyst
particles, followed, under some conditions, by particle fracture. In this
experimental study, individual Shell 405 catalyst particles of various size
and history were mounted in a flow reactor in which the effects of hydrazine
temperature, flow velocity, and exposure time on wetting and breakup could be
determined.

Particle wetting has been found to be strongly controlled by liquid
hydrazine temperature; greatest wetting and most frequent breakup occur in
particles exposed to lowest hydrazine temperatures. Wetting and breakup,
however, are also dependent upon size and history. Both wetting and breakup
vary with as-received particle size. For catalysts heated in an inert atmo-
sphere, apparently independent changes in wetting and breakup can be induced
by various heating conditions, reflecting the complex relationship of the
catalytic surface, pore characteristics and substrate strength.

Tests of catalyst exposed to contaminants or decomposition product poi-
sons indicated that in most cases activity was decreased and breakage was
increased. However, a surprising result of treatment by hydrogen gas was a
marked reduction in breakage accompanied by very small reduction in activity.

The effects of thermal shock and thermal cycling were examined in a
series of screening tests by rapid heating and cooling of particles. Single
and multiple cycles were applied to individual particles. Particle fracture
occurred only under the most severe cooling conditions.

I. INTRODUCTION

The use of hydrazine catalytic reactors for a wide variety of extended life missions is presently limited by degradation of the catalyst particles as evidenced by breakup of the particles. Fracturing of a catalyst particle can be caused by large pressure gradients or thermal stresses within the particle which cannot be supported by the porous structure. Breakup caused by large pressure gradients has been illustrated under conditions in which liquid hydrazine wetting the outside surface of catalyst particles blocked the escape of gaseous decomposition products (Refs. 1 to 3). Wetting by the very reactive hydrazine results in gaseous decomposition product buildup near the gas-liquid interface. Pressure buildup is very rapid, while dissipation of pressure throughout the particle is slow because of the very small pore sizes and correspondingly high pressure drops. Pressure can be alleviated if (a) gas pushed liquid out of the pores, (b) gas escapes from the pores which have not been wet, or (c) the particle fractures. The greater the tendency of the particle to wet and the higher the fraction of the particle which is wet, the more likely the particle is to fracture. In this study, particle wetting has been shown to be related directly to catalyst reactivity in hydrazine. For a given catalyst particle, reactivity increases markedly with temperature since the liquid hydrazine vapor pressure is very sensitive to temperature and it is the vapor which decomposes on the catalyst surfaces. For a set of particles, wetting is associated with the intrinsic activity of each of the particles -- the lower the activity, the greater the likelihood of wetting. Breakup caused by wetting and internal pressure buildup was found to be an important mechanism which is influenced by many factors, particularly liquid temperature, particle activity and particle history.

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1. Sangiovanni, J. J. and A. S. Kesten: Analysis of Gas Pressure Buildup within a Porous Catalyst Particle which is Wet by a Liquid Reactant. Chemical Engineering Science 26, 533-547, 1971.
2. Kesten, A. S.: A Conceptual Model of Hydrazine Catalytic Reactor Washout Caused by Decomposition Product Poisoning and Pressure Buildup. Presented at the Monopropellant Propulsion Specialist Session, JANNAF Propulsion Meeting, New Orleans, La., November 28, 1972.
3. Sangiovanni, J. J. and A. S. Kesten: Motion Picture Studies of the Start-up Characteristics of Liquid Hydrazine Catalytic Reactors. AIAA Paper 71-102, AIAA/SAE 7th Propulsion Joint Specialists Conference, 1971.

Screening of other possible breakup mechanisms was also conducted using both experimental and analytical techniques. The effect of nonuniform wetting on breakup was examined analytically. The effect of thermal stress or thermal fatigue on particle breakup was determined by subjecting individual particles to heating and cooling cycles. In thermal shock tests, particles were heated by a laser and quenched in water, thereby creating large thermal stresses. In thermal cycling tests, heating by laser and cooling by low-temperature gas were alternated for various numbers of cycles. These mechanisms were found to be of much less significance.

The report is divided into three major parts. In the first part, liquid immersion tests are described, and the results are discussed for major categories of particles; as-received, engine-fired, sintered, and contaminated catalysts. In the second section, techniques and results of thermal cycling tests are presented. In the final part, conclusions from both phases of the program are presented and, because several aspects of the program produced unexpected and potentially important results, specific recommendations for future work are listed.

II. LIQUID IMMERSION TESTS

Experimental Apparatus and Procedures

Liquid Immersion Reactor

In order to establish the relationship between wetting and breakup and the dependence of these phenomenon on catalyst size and history, it is preferable to observe the behavior of individual particles. The reactor system shown in Fig. 1 was designed for this purpose.

Shell 405 catalyst particles were exposed to hydrazine in the flow reactor shown schematically in Fig. 2. The body, internal parts, plumbing lines, and valves were stainless steel. A Teflon particle support and EPR O-rings were used; the viewing window was Pyrex. Hydrazine was stored in a 2 liter stainless steel cylinder, pressurized with nitrogen, and metered through Matheson series 600 flow-meters. The hydrazine inlet line was maintained at reactor temperature.

The Teflon particle support rested in the holding fixture; particles were mounted with contact cement. A sliding sheath was dropped over the particle support to isolate the particles from the remainder of the reactor; gases in the particle volume were evacuated through a cold trap by a mechanical pump while reactor temperature was stabilized. Hot and cold tap water were generally used to determine reactor temperature; for runs initially below cold water supply temperature, a circulating cooling bath was installed with 3-way valves to permit switching after test initiation. The reactor temperature and liquid hydrazine temperature were measured with stainless steel-sheathed chromel-alumel thermocouples read directly on Omega readout meters.

The entire conduct of a test could be observed through the viewing window. Motion pictures were taken using a Locam 16 mm camera with type 7241 Ektachrome film at framing rates of 50 to 500 frames per second, giving 80 to 8 seconds elapsed time, respectively. An f/1.8, 50 mm camera lens with 30 mm extension was used to gain image size with acceptable depth of field. A pair of zirconium arc lamps was used for illumination.

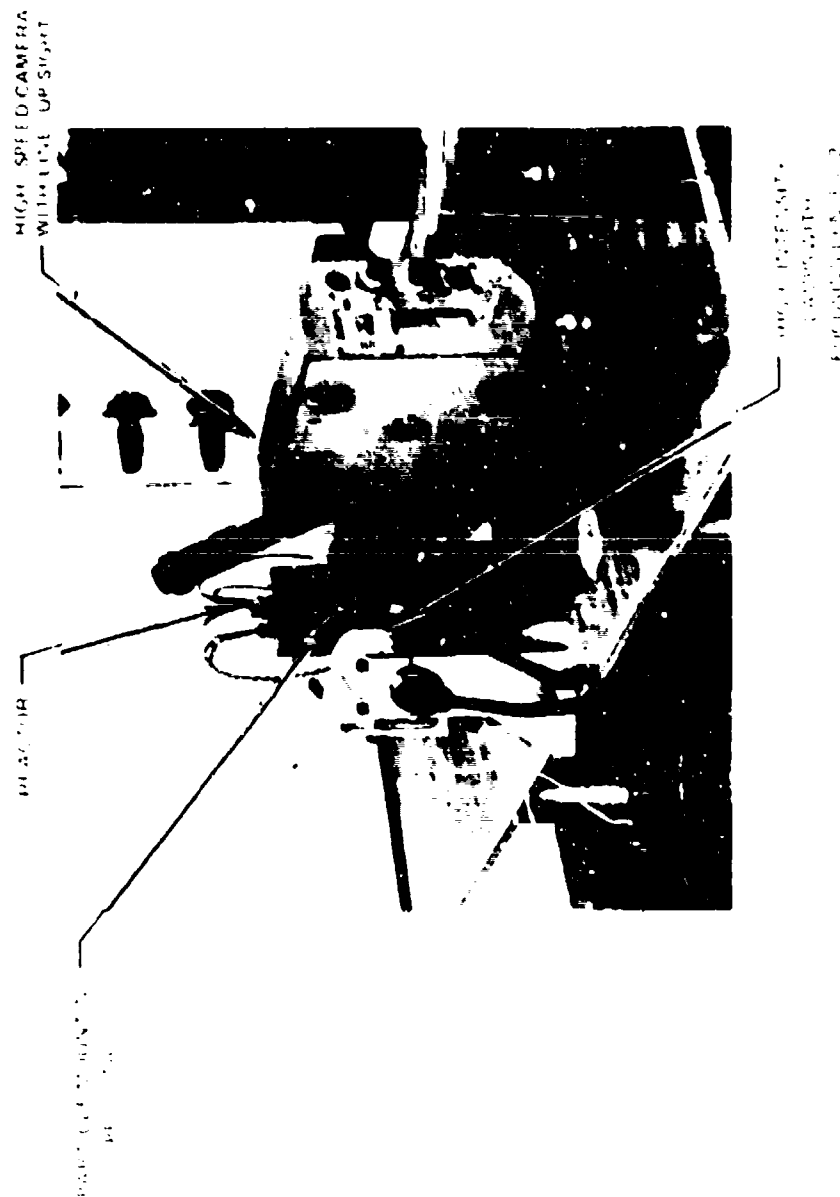REACTOR AND ASSOCIATED APPARATUS FOR STATIC PARTICLE TESTS

FIGURE 1

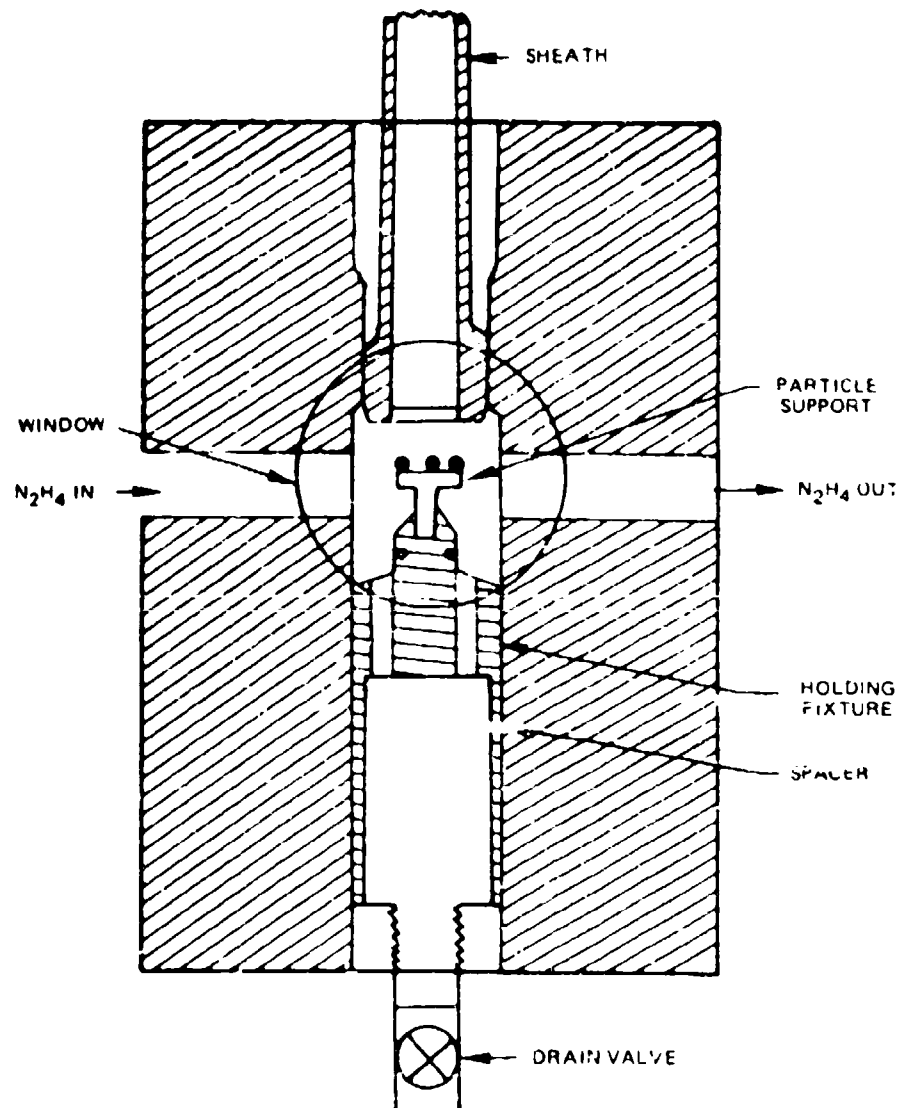## SCHEMATIC DIAGRAM OF REACTOR

FIGURE 2

When reactor temperature was stable, the particle volume was opened to atmospheric pressure, partially filled with mercury, and capped. Hydrazine flow was initiated and held a short time for purging. The camera, run at 500 frames per second, was manually started as the sheath was lifted. Shortly after exposure of particles to liquid, the camera was stopped and reset for 50 frames per second.

Reactor temperature was slowly raised with short film segments taken at temperature intervals of 5 to 10 F. When it appeared that any particle was nearing transition from wetted to unwetted state, film was continuously run. The transition temperature and breakage (if any) of each particle were recorded.

This general procedure was used for all liquid immersion tests. Initial temperatures were usually 10 to 20 degrees below the transition temperature and were as low as 31 F; maximum temperature of the water-heated reactor was approximately 110 F.

Particles of three sizes and a variety of histories were tested. As-received particles of 8-12, 14-18, and 20-30 mesh size were used. As-received samples were heated in inert atmospheres to determine the effect of heating on wetting and breakup, and as-received particles were exposed to gaseous contaminants just before testing in the liquid immersion reactor. Catalyst which had been exposed to contaminants added to hydrazine fuel in a previous contract at UTRC (Ref. 4) was tested, and the Air Force Rocket Propulsion Laboratory supplied samples of 14-18 mesh catalyst taken from a test engine (Ref. 5).

Particle Heating

Heating of as-received catalyst was conducted under an argon atmosphere in an electric furnace having a ceramic tube liner. Ends of the tube were

4. Christopher, G. L. M. and S. Russell: Contamination Effects on Catalyst Life. Report AFRPL TR-74-38, presented by United Technologies Research Center (formerly United Aircraft Research Laboratories), July 1974.
5. Quirk, J. A.: Hydrazine Engine Cold-Start Evaluation. CPIA Publication No. 260, Vol. I, Part II, p. 447, JANNAF Propulsion Meeting, 1974.

sealed to fittings to accommodate either a small flow of gas or connection
to vacuum. Samples were loaded into ceramic boats for heating. Heating
times were varied from one-half hour to overnight at temperatures of 375 F
to 1400 F. For heating times of 2 hr or longer at 500 to 1000 F, samples
were loaded into a cold furnace and left in place during heatup, soak and
cooldown. For shorter times at temperatures of 375 and 500 F, samples were
loaded directly into the heated furnace, then moved after the appropriate
time to a cool section of the ceramic tube, and, after further cooling,
removed from the liner. Argon flow was maintained while samples were in the
heating tube, except for one instance of heating in vacuum at 500 F. Cooled
samples were stored in stoppered glass vials.

Catalyst Contamination

Samples were exposed to potential gaseous contaminants (hydrazine decom-
position products) by introducing nitrogen, hydrogen or ammonia gas to the
sample volume after particles had been placed in the test reactor and the
volume was evacuated. The gases were admitted at 50 psig for 10 minutes,
after which the volume was evacuated, vented to atmospheric pressure and
backfilled with mercury.

The liquid phase contamination was conducted during a previous contract
at UTRC (Ref. 4). Catalyst was exposed to contaminants in a flow reactor
using hydrazine to which aniline, iron, or zinc were added. Pure fuel was
utilized for 10 sec, the mixture was used for 300 sec, and pure fuel was
employed for an additional 10 sec. Samples used in current tests were
removed from the upper (injector) section of the flow reactor.

Catalyst removed from the thruster tests at AFRPL (Ref. 5) had been sub-
jected to 98 cold starts and 166 hot starts, with a total of 115,673 pulses.
Samples coded U >30 consisted of 20-30 mesh catalyst removed from the upper
bed; samples of 14-18 mesh catalyst, coded L >25, were taken from a lower bed
location.

Results and Discussion
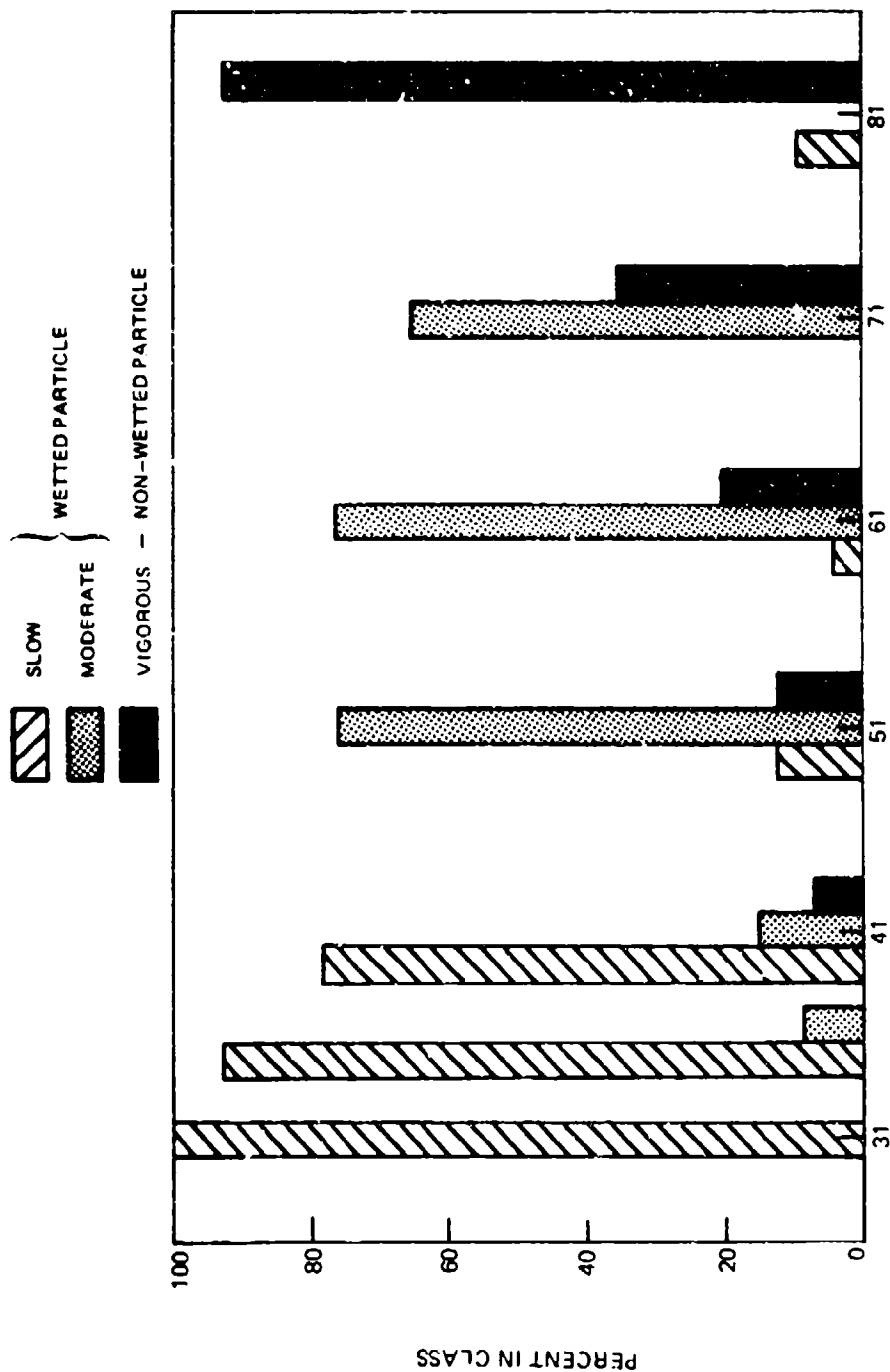
As-Received Particles

In the course of testing catalyst particles, observations were made of the following: vigor with which gas was evolved by each particle, changes in the character of evolution, the temperature dependence of such changes, and breakage of particles. The most important factors determining wetting and breakup were found to be the hydrazine temperature, particle size and particle history.

In view of the temperature dependence of hydrazine vapor pressure, it would be expected that lowest gas evolution for any given batch of catalyst would be observed at lowest temperatures. This was found to be true for each catalyst batch; an illustration is given in Fig. 3. The rate of gaseous evolution upon initial exposure was qualitatively classified as slow, moderate or vigorous. Slow evolution was characterized by low-energy ejection of bubbles of diameter much smaller than the particle; moderate evolution corresponded to greater quantity of somewhat more energetic bubbles which moved from the particle in a plume. Vigorous evolution was characterized by large bubbles of diameter comparable to the particle diameter; these left the particle individually with much higher velocity. The particle remained well-defined in the first two classes of evolution but was almost completely obscured by a vapor film and gas bubbles in the case of vigorous evolution. Thus, the first two cases appear to correspond to wetted particles, and vigorous evolution typifies nonwetted particles.

The increasing activity vs temperature, as illustrated in Fig. 3, was associated in each batch with a second characteristic termed the transition temperature. If the reactor temperature was raised after first exposure, activity of particles in the first two classes increased. The increase in activity of particles in the slow and moderate classes was gradual and steady. However, within a temperature interval characteristic of each batch, moderate particles abruptly became vigorous. The interval over which this occurred was sufficiently narrow that a change in the rate of gas decomposition caused by an increase in hydrazine vapor pressure was not possible. This transition thus marks a change in degree of wetting and pressure buildup, rather than a change in the character of gas evolution. Below this transition temperature, particles are largely wetted and gas escapes from individual pores in small bubbles. Above the transition temperature there is essentially no wetting. The particle is surrounded by evolved gas; the products formed within the vapor film escape as large bubbles.

EFFECT OF LIQUID TEMPERATURE ON INITIAL ACTIVITY OF PARTICLE

CATALYST – LOT 10 - MEM 20–30 MESH, AS RECEIVED

FIGURE 3

Although a characteristic transition temperature was found for each batch of catalyst, the transition temperature is not precisely the same for all particles of one batch. The distribution of transition temperatures for the same catalyst tests reported in Fig. 3 is given in Fig. 4. While a relatively narrow temperature range encompasses most particles, it is clear that particles of varied characteristics are found in each sample. Even under uniform conditions, therefore, a particle-to-particle variation in wetting will result from the difference in intrinsic characteristics.

The final observation in each test was of particle breakup. Some particles broke upon first exposure; others broke upon heating, and some did not break. Breakup was always found to be associated with transition; particles which broke upon first exposure were also vigorous on first observation. In addition, remnants of broken particles exhibited vigorous evolution.

Particles which were exposed at low initial temperatures were found to be more susceptible to breakup on reactor heating. Data representing particle breakup are shown in Fig. 5 and listed in Table 1. The fraction of particles breaking upon heating is high for low initial temperatures and decreases as the exposure temperature approaches the transition temperature.

A logical picture of particle reactivity emerges from these observations. Particles which are very low in reactivity, although they may be wetted, do not undergo a high rate of internal pressure buildup, because the rate of escape of gas from large pores is adequate to minimize internal forces. The very reactive particles generate gas near the surface rapidly enough to prevent wetting. In this instance, the internal pressure also does not rise. In intermediate cases, however, partial wetting can cause the rate of evolution of gases to exceed the rate of escape and the internal forces can build, causing breakup. When particles break, the newly exposed surfaces do not wet since the internally-trapped gases provide a vapor film, and the vigorous type of evolution results.

The important effect of initial temperature arises from the probability of wetting in discrete areas, rather than uniformly. At lower initial temperatures, a greater fraction of the surface will be wet since fewer areas of the particle can generate gas rapidly enough to prevent capillary intrusion. As the temperature is raised, however, the blocked pores tend to remain blocked until high internal pressures are attained.

The results of further tests on this and other as-received catalyst batches are summarized in Table 2. The sum of the results indicates that each batch of catalyst has an essentially unique transition temperature and a specific rate of breakage which reflects a balance in the particle activity and strength.

DISTRIBUTION OF PARTICLE TRANSITION TEMPERATURES
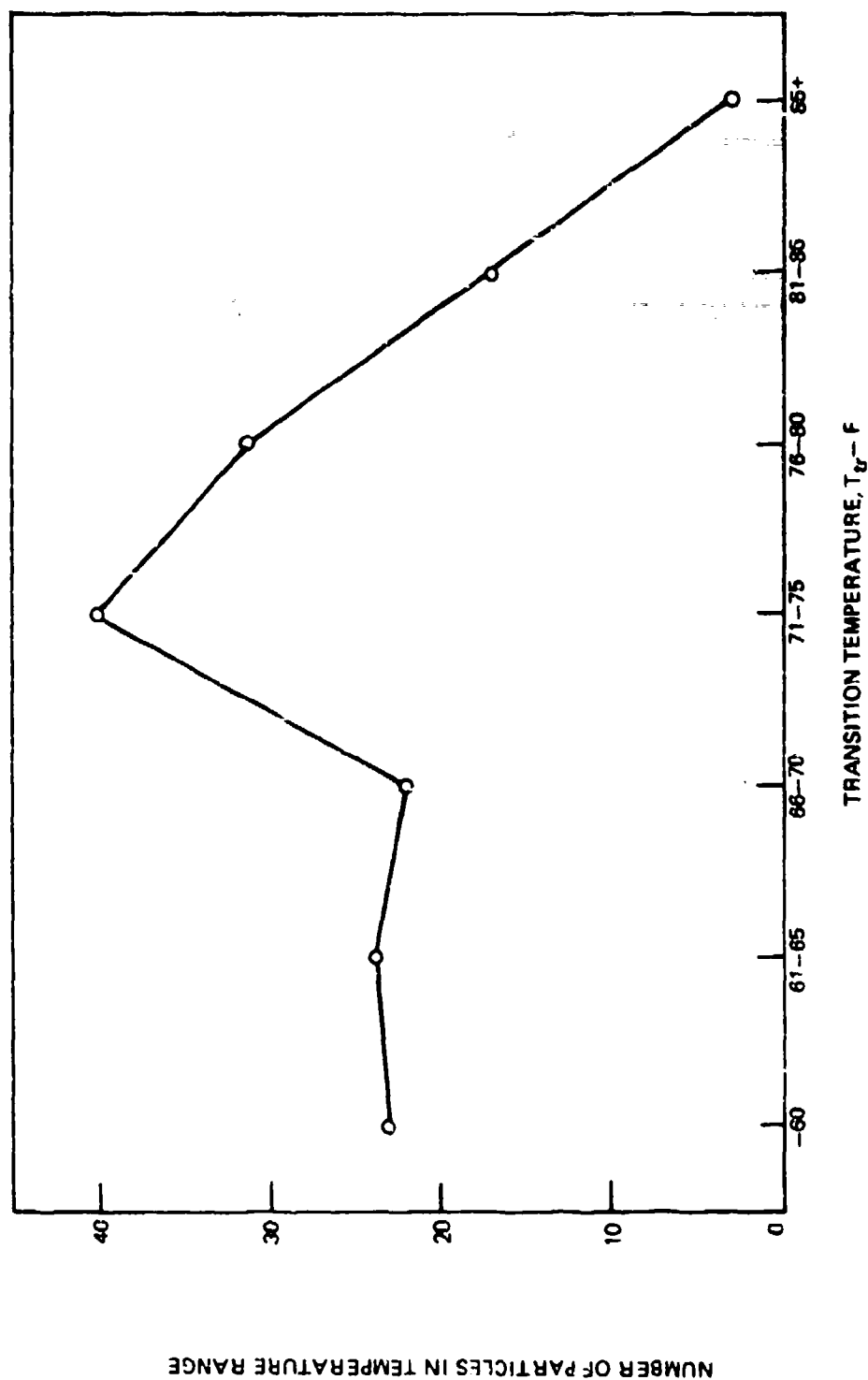
CATALYST – LOT 10 –MEM 20 –30 MESH, AS RECEIVED

FIGURE 4

EFFECT OF HYDRAZINE TEMPERATURE ON BREAKAGE UPON HEATING

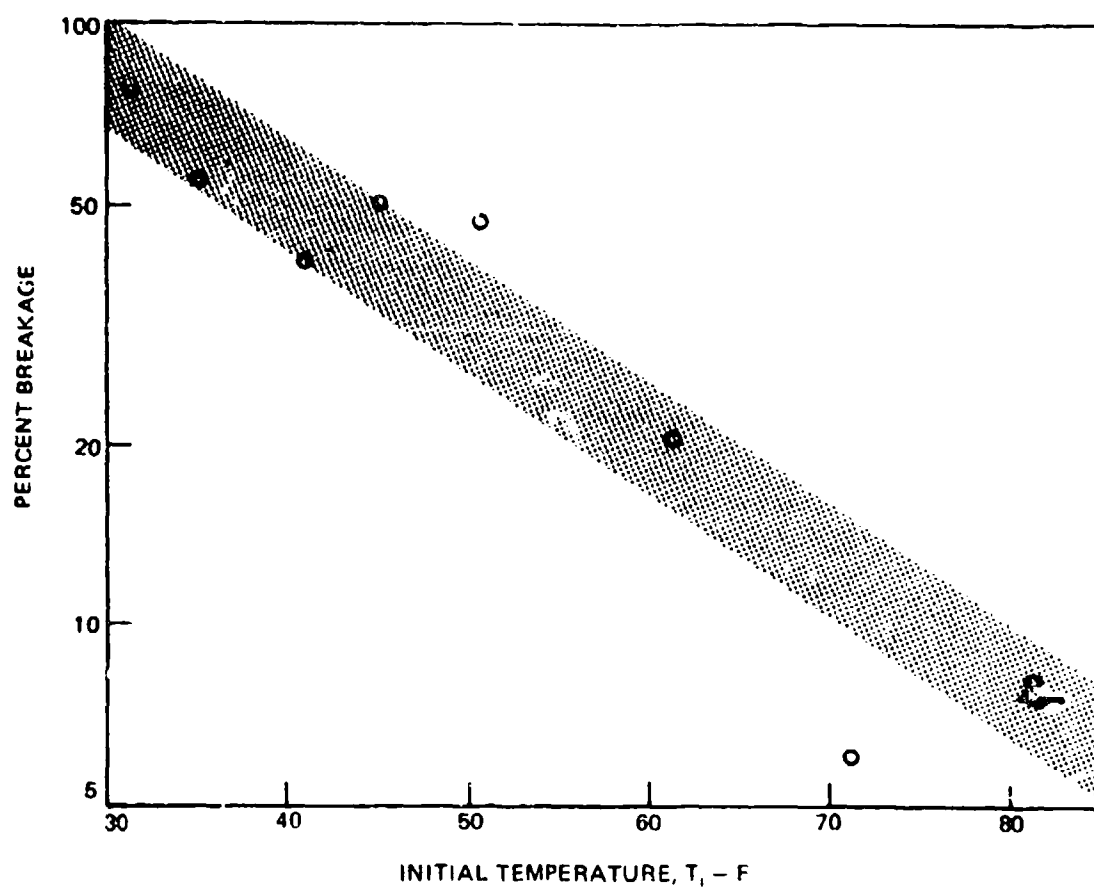CATALYST — LOT 10 - MEM   20--30 MESH, AS RECEIVED

INITIAL TEMPERATURE, T_i — F

FIGURE 5

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TABLE 1

EFFECT OF INITIAL TEMPERATURE
ON PARTICLE BREAKUP

Catalyst 20-30 Mesh Shell 405 Lot 10-MEM as-received
Hydrazine - Mil Spec. Velocity 8 ft/sec

Initial Reactor Temperature, F	No. of Runs	Initial Evolution	Particles Breaking		Transition Temperature	
			Initially	Upon Heating	Range	Average
32	18	18-slow	0	14	50-83	65
35	22	21-slow	0	11	60-80	71
		1-moderate	0	1	60	60
		0-vigorous	0	0	-	-
41	27	21-slow	0	9	43-90	73
		4-moderate	0	3	60-96	73
		2-vigorous	1	0	-	41
51	17	2-slow	0	1	70-75	73
		13-moderate	0	7	60-85	73
		2-vigorous	1	0	-	51
61	25	1-slow	0	0	74	74
		19-moderate	0	5	62-85	74
		5-vigorous	0	0	-	61
71	17	0-slow	0	0	-	-
		11-moderate	0	1	72-85	70
		6-vigorous	0	0	-	71
81	12	1-slow	0	1	90	90
		0-moderate	0	0	-	-
		11-vigorous	0	0	-	81

TABLE 2

TRANSITION TEMPERATURES AND BREAKUP OF
AS-RECEIVED AND ENGINE-FIRED
SHELL 405 CATALYST

Catalyst Sample	Initial Reactor Temperature, F	Transition Temperature, F	Number (Fraction) Breaking
8-12 Mesh Lot 4-MEM (As-received)	32	32	0/27 (0)
14-18 Mesh Lot 12-MEM (As-received)	41	42	4/33 (0.12)
Lot 6-LEM (As-received)	32	32	0/9 (0)
AFRPL L > 25 (Engine-fired)	41	62	20/27 (0.74)
20-30 Mesh Lot 10-MEM (As-received)	41	62	27/48 (0.58)
Lot 10526 (As-received)	41	65	2/15 (0.13)
Lot 12-MEM (20-24 Mesh)	41	54	7/18 (0.39)
AFRPL U > 30 (Engine-fired)	61	92	6/48 (0.13)
Lot 6-PEN (As-received)	41	55	3/23 (0.13)
Lot 7-QHO (As-received)	41	55	4/21 (0.19)

An important conclusion from those results is that any active particle could, in principle, be broken if initial wetting were sufficiently complete to block gas escape as the liquid temperature rose.

A surprising result is illustrated by Table 2. Both transition temperature and breakage are found to increase with decreasing particle size. That is, smaller particles are more readily wet and are more susceptible to breakage. Although the relationship between activity and breakage is consistent in all as-received samples, no clear reason for the trend has been apparent. In order to test the effect of particle size on characteristics, samples of Lot 12-MEM (14-18 mesh) were crushed between steel plates, screened to 20-24 mesh, and tested in the liquid immersion reactor. Both transition temperature and breakup increased, in line with the trend shown by as-received catalysts.

One question of interest has been whether breakage statistics hold for each immersion of particles; that is, do those particles breaking on initial exposure represent inherently weaker substrates. In order to explore this point, particles were left in the reactor for a second exposure to hydrazine.

The conduct of these tests is complicated by the necessity to drive both liquid and vapor hydrazine away from the particles rapidly, since it has been found that particles exposed to hydrazine vapor have become luminous from reaction heat and are probably sintered. In one series, nitrogen gas was used to clear the reactor of both liquid and gaseous hydrazine, after which the particle sheath was lowered, the particle volume was reevacuated, and the particle was retested. In other tests, the hydrazine level was dropped by gravity, the sheath was lowered, and hydrazine vapor was pumped away preparatory to retest. These results were not conclusive. The average transition temperature was 71 F, higher than the 63 F for as-received particles, but breakage was almost nil (1 of 36 particles broke). The average transition temperature change indicates that a net activity decrease occurred, and this would be expected to lead to higher breakage. However, the distribution of particle transition temperatures was unusual; some particles remained very active, and would not be expected to break. Others became much less active, possibly due to sintering; these would also be less prone to breakage because of slow pressure buildup.

A return to testing methods of previous work at CRC (Ref. 3) may be indicated for tests of this type. In previous tests the catalyst particle

was elevated from and lowered back into a mercury pool below liquid hydrazine. This provides sufficient heat transfer that particles returned to mercury would remain cool; however, the problem of adequate removal of decomposition products from the particle remains.

Several parameters were found to have little effect on wetting or breakup in single particle tests. Flow velocity was found to affect the shape and velocity of the plume of evolved gases, but not the apparent rate of evolution. This reflects the fact that the capillary intrusion caused by surface tension involves pressures much greater than the dynamic pressure of the hydrazine stream. In packed bed reactors, however, liquid velocity determines the penetration depth of liquid into the bed. Therefore, the total number of particles which may potentially be wet and break is dependent upon velocity.

A simplified thin slab model of a porous catalyst particle has been used to make an assessment of the importance of nonuniform wetting on stressing of the particle structure. If the model catalyst particle were wet by liquid hydrazine on one side only, with the other side exposed to hydrazine vapor, the latter side could heat up due to hydrazine decomposition while the wet side would remain cooled by the liquid. The resulting temperature gradient would result in thermal stress acting to increase the stress caused by pressure buildup at the liquid interface. The significance of this additional stress was estimated by computing the temperature rise of the "dry" side of the model particle during the period of pressure buildup due to wetting of the other side. Computations were made as a function of liquid temperature with the vapor hydrazine at a concentration determined by the vapor pressure at the liquid temperature. Temperature rises of only a few degrees were calculated at liquid hydrazine temperatures of interest. This would indicate that enhancement of pressure stress by heating resulting from nonuniform wetting is small.

Engine-Fired Samples

The results of tests on engine-fired sample forwarded by AFRPL (Ref. 5) are also given in Table 2. A 14-18 mesh sample (L > 25, removed from a lower bed), when tested at 71 F, resembled as-received 14-18 mesh samples at approximately 37 F. That is, there was a moderate range of initial activitites, accompanied by significant breakage upon heating. It would appear that the engine-fired catalyst has suffered a significant reduction in activity, i.e., a higher reaction temperature is required for equivalent gas evolution. This could account for greater breakage at equal initial temperatures, by virtue of

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much greater initial wetting. A factor which may coexist is weakening of the substrate by other mechanisms.

Similar differences in activity were noted between as-received 20-30 mesh particles and engine-fired 20-30 mesh catalyst from an upper bed (U > 30). However, a much smaller fraction of used 20-30 mesh particles broke upon heating even though the transition temperatures were very high. The contrast between AFRPL L > 25 and U > 30 samples may be due to differences in the balance of activity, physical characteristics and strength of particles. The possibility of liquid completely filling part of the porous structure of the apparently inactive U > 30 particles and retarding breakup must be considered

Several aspects of the engine-fired particles were distinctly different from previously-conducted tests. First, the bubbles of gas products appeared to be smaller than for as-received particles. Secondly, the transition from slow to vigorous conditions was less abrupt. Thirdly, the particles generally fractured by simple splitting rather than exploding in a burst of fragments. Finally, at the temperatures of 61 or 71 F, particles which were classified as initially vigorous included some which required a short induction period of approximately 1 second or less.

These observations are consistent with a picture of lower activity, especially near the surface, possibly coupled with an altered pore size distribution or reduction in substrate strength. As a result of lower activity, slightly longer time might be required to build up internal gas pressure and expel liquid; this would correspond to the induction phase. Increase in average pore size would be reflected in facilitated pressure release; reduction in substrate strength may be responsible for the less spectacular breakage.

Heated Catalyst

The results on as-received and engine-fired particles indicate that factors beyond intrinsic activity are important. The pore sizes and pore size distributions play an important role in determining the degree of wetting, the magnitude of internal pressure rise, and the differential pressure stresses across pore walls. Changes in these particle characteristics can be induced by heating. Particles were subjected to a wide range of heating temperatures and times to determine the effect of heating on the relationship between wetting and breakup.

The results of heating as-received particles are given in Tables 3 and 4. Data in Table 3 pertain to heating 14-18 and 20-30 mesh catalyst for times of 2 hrs at temperatures of 500 to 1400 F. Data in Table 4 present the results of heating 20-30 mesh catalyst for various times at low temperatures. The

TABLE 3

TRANSITION TEMPERATURES AND PARTICLE BREAKUP IN SHELL 405 CATALYST AFTER HEATING IN ARGON: EFFECT OF TEMPERATURE

Sample Treatment	Transition Temperature	Number (Fraction) Breaking
14-18 Mesh, Lot 12-MEM		
As-received	42	4/33 (0.12)
500 F, Argon, 2 hr	71	0/15 (0)
950 F, Argon, 2 hr	110	1/12 (0.08)
1400 F, Argon, 2 hr	110	0/12 (0)
20-30 Mesh, Lot 10-MEM		
As-received	63	27/48 (0.56)
500 F, Argon, 2 hr	89	1/15 (0.07)
500 F. Vacuum, 2 hr	81	1/13 (0.08)
950 F, Argon, 2 hr	110	0/12 (0)
1400 F, Argon, 2 hr	110	0/12 (0)

TABLE 4

TRANSITION TEMPERATURE AND PARTICLE BREAKUP
IN SHELL 405 CATALYST AFTER HEATING IN ARGON:
EFFECT OF HEATING TIME

Catalyst: 20-30 Mesh, Lot 10-MEM

Treatment	Transition Temperature, F	Number (Fraction) Breaking
As-received	63	27/48 (0.56)
1/2 hr, 375 F	62	3/14 (0.21)
1 hr, 375 F	63	3/15 (0.20)
1 1/2 hr, 375 F	62	3/15 (0.20)
2 hr, 375 F	63	4/16 (0.25)
Overnight, 375 F	64	4/17 (0.24)
1/2 hr, 500 F	69	1/15 (0.07)
1 hr, 500 F	67	1/15 (0.07)
1 1/2 hr, 500 F	68	2/15 (0.14)
2 hr, 500 F	89	2/21 (0.10)
Overnight, 500 F	97	2/15 (0.13)
2 hr, 375 F	63	4/16 (0.25)
2 hr, 500 F	89	2/21 (0.10)
2 hr, 950 F	110	2/12 (0.17)
2 hr, 1400 F	110	0/12 (0)

effect of heating at temperatures of 500 F or above was to raise the transition temperature of samples (i.e., decrease the activity) and decrease breakage to a low level. However, the first treatment was found to have the greatest effect on reduction of breakage. This was particularly true for the 20-30 mesh sample where breakage after heating at 500 F was reduced by a factor of approximately 8.

In addition to the very large reduction in breakage, the relationship between transition temperature and breakage no longer follows the trend for as-received particles. The great change in breakage would be expected to be accompanied by a much larger change in transition temperature than is observed, or the more gradual change in transition temperature should be accompanied by smaller and incremental changes in breakage.

To test whether intermediate change, might be possible, further heating was conducted on Lot 10-MEM (20-30 mesh), which had the largest breakage for as-received catalyst; samples were heated for short times at 375 and 500 F. These results are shown in Table 4. The results to some extent parallel the data shown in Table 3, and similarly do not match the trend for as-received samples. Heating at 375 F produced a very slight increase in particle activity and a marked decrease in breakage. Heating at 500 F produced a small activity decrease for heating times to 1-1/2 hrs and larger decrease thereafter: this was accompanied by a significant decrease in breakage beyond the 375 F ase.

These results indicate that particle activity alone is not representative of breakage to be expected, since greatly reduced breakage may accompany slight change in activity. The most probable alteration which occurs during heating is a shift in average pore size to greater diameters through the mechanism of pore coalescence or unblocking; this could lead to lower breakage through easier pressure release. It is possible that small changes in catalytic area, not reflected in evolution, accompany initial pore changes. However, as pore size is increased by coalescence (i.e., as pore area decreases) catalyst active area must also ultimately decrease.

Contaminated Catalysts

The effect of contamination on particle characteristics was determined using samples contaminated by several procedures. One class of contaminated samples exposed to impurities or foreign substances found in hydrazine, was prepared during a previous contract at UTRC (Ref. 4). In that effort, contaminants were deposited from hydrazine fuel during continuous-flow reactor

runs lasting 300 sec. The contaminants were aniline, added to Mil Spec hydrazine at concentrations of 25,000, 50,000, and 100,000 ppm, iron (as ferric nitrate) at 500 ppm and zinc (as zinc nitrate) at 500 ppm. Samples tested in the liquid immersion reactor during this report period had been removed from the injector portion of the flow reactor. As-received samples of the catalyst used in the contamination studies were tested for reference. The results are given in Table 5.

A great variation in the effect of contamination from the fuel was found. Aniline had a moderate effect on characteristics, while iron and zinc showed strong effects. The transition temperature of samples exposed to the 25,000 ppm aniline/hydrazine mixture was the same as for the as-received sample, i.e., 55 F. The transition temperature was 60 F for the 50,000 ppm mixture and slightly higher, 61 F, for the 100,000 ppm mixture. Breakage was more extensive for the 25,000 ppm mixture than for as-received catalyst, and breakage declined with increasing aniline concentration, but remained above that of as-received samples.

The effect of iron and zinc poisons was much more pronounced. Both samples had significantly higher transition temperatures and breakage. In addition, some catalyst was found to be essentially inert; 7 of 18 zinc and 1 of 15 iron-contaminated particles showed negligible activity at all reactor temperatures to 110 F. The character of the gaseous evolution from these samples was also unusual. The reaction sometimes appeared to be sporadic; a clear transition to vigorous activity was occasionally followed by relaxation to lower activity. In the case of zinc-contaminated catalyst, transition to vigorous activity was less clear and the rate of evolution after transition appeared to be lower than for the iron-contaminated catalyst or as-received samples.

The samples used in these tests, as noted above, were prepared by contamination from liquid hydrazine in a flow reactor. Although the contaminant level was constant during the 300 sec firing, not all particles within each of the three bed locations would be expected to reflect the same degree of contamination. Particle orientation and location with respect to the fuel flow, local particle temperatures and remaining contaminant in the flow all would determine the deposit on individual particles. In addition, a 10 sec run with pure hydrazine was conducted at the end of each 300 sec firing; some contaminants may have been removed during this period. Thus, wide intra- and inter-particle variation could be expected.

A second class of contaminated sample was prepared by introducing nitrogen, hydrogen or ammonia gas to the sample volume after particles had been placed in the reactor and the volume was evacuated. These gases represent potential catalyst poisons which are produced by the hydrazine decomposition. The gases

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TABLE 5

TRANSITION TEMPERATURES AND PARTICLE BREAKUP
IN AS-RECEIVED AND SOLUTION-CONTAMINATED
20-30 MESH SHELL 405 CATALYST

Batch	Contaminant		Transition Temperature	Number (Fraction) Breaking
7-QHO	As-received		55	4/21 (0.19)
7-QHO	Aniline	25,000 ppm in hydrazine	55	6/15 (0.40)
7-QHO	Aniline	50,000 ppm in hydrazine	60	5/15 (0.33)
7-QHO	Aniline	100,000 ppm in hydrazine	61	4/15 (0.27)
6-PEN	As-received		55	3/23 (0.13)
6-PEN	Zinc	500 ppm in hydrazine	86	6/18 (0.33)
		discounting inactive catalyst	71	6/11 (0.55)
6-PEN	Iron	50 ppm in hydrazine	65	6/15 (0.40)
		discounting inactive catalyst	62	6/14 (0.43)

Note: Contaminants applied from hydrazine solution during tests at UTRC under
Contract F04611-73-C-0019 (Ref. 4).

were admitted at 50 psig for 10 minutes, after which the volume was evacuated, vented to atmospheric pressure and backfilled with mercury. These treatments were applied to as-received samples of Lot 10-MEM, used in most liquid immersion tests to date, and to as-received samples of Lot 7-QHO, used in the liquid contamination studies (Ref. 4). The as-received batches have somewhat different characteristics; Lot 7-QHO exhibits a lower temperature and much lower breakage than Lot 10-MEM. The results of these tests are shown in Table 6.

Treatment of Lot 10-MEM with nitrogen gas produced no distinct change in particle characteristics. Both the transition temperature and breakage remained similar to those of as-received samples, and the general character of the evolution was unchanged from the as-received sample. Hydrogen and ammonia treatment produced significant but different changes. Hydrogen treatment resulted in elimination of breakage without change in transition temperature, while ammonia caused an increase in breakage which was accompanied by an increase in transition temperature. Ammonia-treated particles also tended to shatter when breaking. The similarity of results in the two batches indicates that these are general processes and not specific to one sample.

Since Shell 405 catalyst is stabilized to air, it would not be expected that exposure to nitrogen at low temperature would produce significant changes in the catalyst. In both current tests and those reported in Ref. 3, nitrogen treatment had no sensible effect. But the effect of hydrogen treatment appears to be remarkable. In Ref. 3, it was reported that hydrogen treatment similar to that of current tests reduced catalyst activity, though the reduction was small for low hydrogen pressures as were used here. In the current tests hydrogen treatment caused no perceptible change in transition temperature, which is related to activity. Certainly, the dramatic reduction of breakage appears unrelated to activity. The only other instance where similar behavior was noted was in the series of heating tests where heating even at low temperature in an inert atmosphere reduced breakage considerably without much change in apparent activity.

Increased breakage after ammonia treatment may reflect both surface activity reduction, which would increase wetting, and physical blockage. The blockage could result from capillary condensation of ammonia in the particle pores. Upon sudden evacuation, freezing of the condensed ammonia could inhibit removal, and the trapped ammonia could remain as liquid during coverage by mercury, remaining in the pores after exposure to hydrazine.

Validation Tests

The validity of experimental procedures was also examined in special tests. In one series, mercury backfill after evacuation was eliminated. The

TABLE 6

TRANSITION TEMPERATURES AND PARTICLE BREAKUP IN AS-RECEIVED AND GAS-CONTAMINATED 20-30 MESH SHELL 405 CATALYST

Batch	Contaminant	Transition Temperature	Number (Fraction) Breaking
10-MEM	As-received	63	27/48 (0.56)
10-MEM	Nitrogen	62	5/11 (0.45)
10-MEM	Hydrogen	63	0/15 (0)
10-MEM	Ammonia	65	11/15 (0.73)
7-QHO	As-received	55	4/21 (0.19)
7-QHO	Hydrogen	55	0/9 (0)
7-QHO	Ammonia	61	4/9 (0.4..)

Note: Contaminants applied for 10 min at 50 psig after loading in liquid immersion reactor.

purpose of testing without mercury backfill was to establish whether mercury
has any effect on the particle surface, either by intrusion or amalgamation.
No change in activity was found; a transition temperature of 64 F for Lot 10-
MEM, as opposed to 63 F for tests with mercury backfill, was observed.
However, lower breakage was observed (30% vs ~ 50%). This indicates that the
mercury does not interact with the catalytic surface, but that the absence of
the surrounding liquid mercury permits approaching hydrazine vapor to react
before liquid hydrazine can significantly interact with the particle.

Long immersion times at fixed temperature also had no effect on activity.
Samples which were low in activity were left in place without heating for as
long as 1000 sec; no increase in activity was found. However, if low activity
particles were exposed to vapor by lowering the liquid, vigorous evolution was
found after reimmersion. Lack of change in evolution under steady wetting is
a result of continued heat transfer to the liquid; in the single particle tests
the liquid temperature did not rise, and evolution remained steady. However,
lowering the liquid simultaneously removes the cooling effect of the liquid,
allowing increasing reaction rate as the particle heats, and reduces the in-
ternal pressure necessary to expel capillary liquid by removing the liquid.
Once particle temperatures and gaseous evolution are increased, reimmersion
cannot quench reaction and vigorous evolution continues.

A third variation in liquid immersion experiments was also conducted over
long time periods. Samples of 8-10 and 14-18 mesh, as-received catalyst were
exposed to temperatures of 41 F; initial reaction was vigorous. The hydrazine
flow was stopped, and the reactor lines were closed. After one-half hour,
reaction in each case had slowed appreciably. However, when pressure was
released and fresh hydrazine was admitted, vigorous reaction was immediately
restored. This was repeated four to six times; each cycle led to the same
result. No breakage accompanied any of the resurgent activity. This may
indicate that an accumulation of dissolved decomposition products inhibited
the reaction, but that wetting did not occur, and intrinsic particle activity
was not diminished.

A final variation in procedure involved the rate of heating of the reactor
system. In this series, the time to raise the reactor temperature from 41 F
to 90 F was extended to approximately 4 hours. The observed transitions and
transition temperatures for 20-30 mesh, as-received particles were similar to
those runs in which heating times of 3 to 5 min were employed. This further
indicates that wetting, gas generation, internal pressure and pore pressure
release are in balance at all temperatures.

III. THERMAL SHOCK AND THERMAL CYCLING TESTS

Experimental Apparatus and Procedures

Thermal shock and thermal cycling tests were conducted using the apparatus shown in Fig. 6. The beam of a CRL Model 40 laser was directed at catalyst particles. In thermal shock tests, the motor-driven system was not activated; the optical path from laser to sample was clear. A firebrick was used to block the beam during sample insertion and was removed manually to initiate heating. Heating rates were approximately 500 to 1000 F persecond; the intention was to attain test temperatures over the same time span, i.e., approximately 2 seconds.

Samples were mounted directly to thermocouple beads with a small quantity of high-conductivity, silver-bearing epoxy cement. The particles were positioned at the focal point of the optical system such that the thermocouple was not in the beam. The sample holder was held in vertical position by a small block; when the desired particle temperature was attained, the block was removed and the sample was pressed downward, plunging the particle into a container of water at 40 F. Separate tests with the thermocouple placed in the beam focus and with a second thermocouple bead (welded to the first) in catalyst position verified the correspondence of particle and thermocouple temperatures, adequate thermocouple response time, and negligible heating of the thermocouple by slight misalignment (the intensity of the laser beam falls off very rapidly away from the central portion).

Particles were subjected to thermal cycling in the laser heating system shown schematically in Fig. 7. A laser beam and liquid nitrogen boil-off jets were alternately directed on the suspended particles. The one-cycle time was approximately 120 millisec, determined by a variable-speed, rotating cylindrical shutter having four open ports of 45 deg each. The axes of the four cooling jets were positioned at 45 deg to the optical axis.

Particle temperatures of over 2000 R could be obtained by steady exposu. to the laser beam; with the shutter rotating and with both heating and cooling systems operating, particle temperatures as high as 1950 R were determined with an optical pyrometer. Thermocouple readout of temperature was obtained for lower cycling rates at both higher and lower temperatures, where response time was less significant.

THERMAL CYCLING AND THERMAL SHOCK APPARATUS FOR CATALYST P/ STUDIES
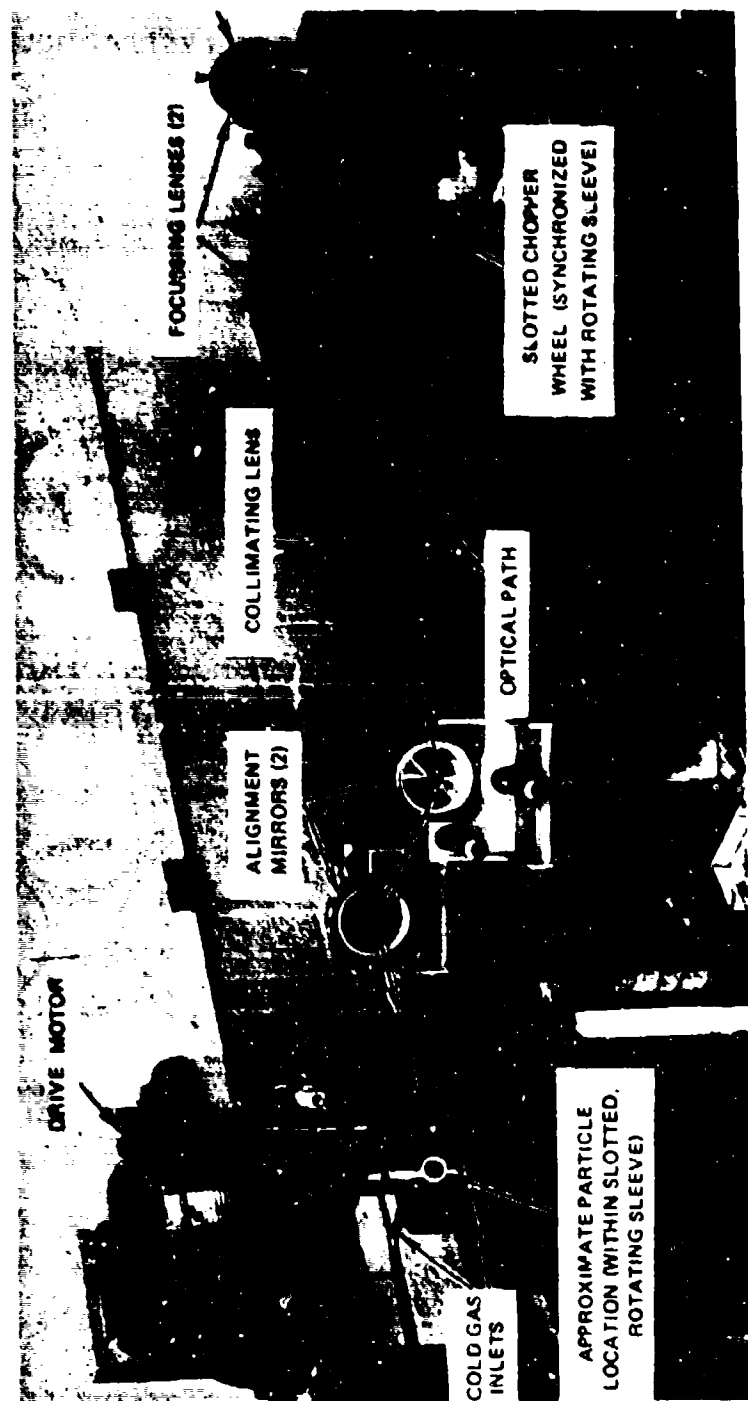
NOTE TRANSMISSION OPTICS NOT MOUNTED

FIGURE 6

THERMAL CYCLING APPARATUS FOR CATALYST PARTICLE STUDIES

CATALYST SUPPORT SYSTEM
(SIDE VIEW)

HEATING CYCLE
(TOP VIEW)
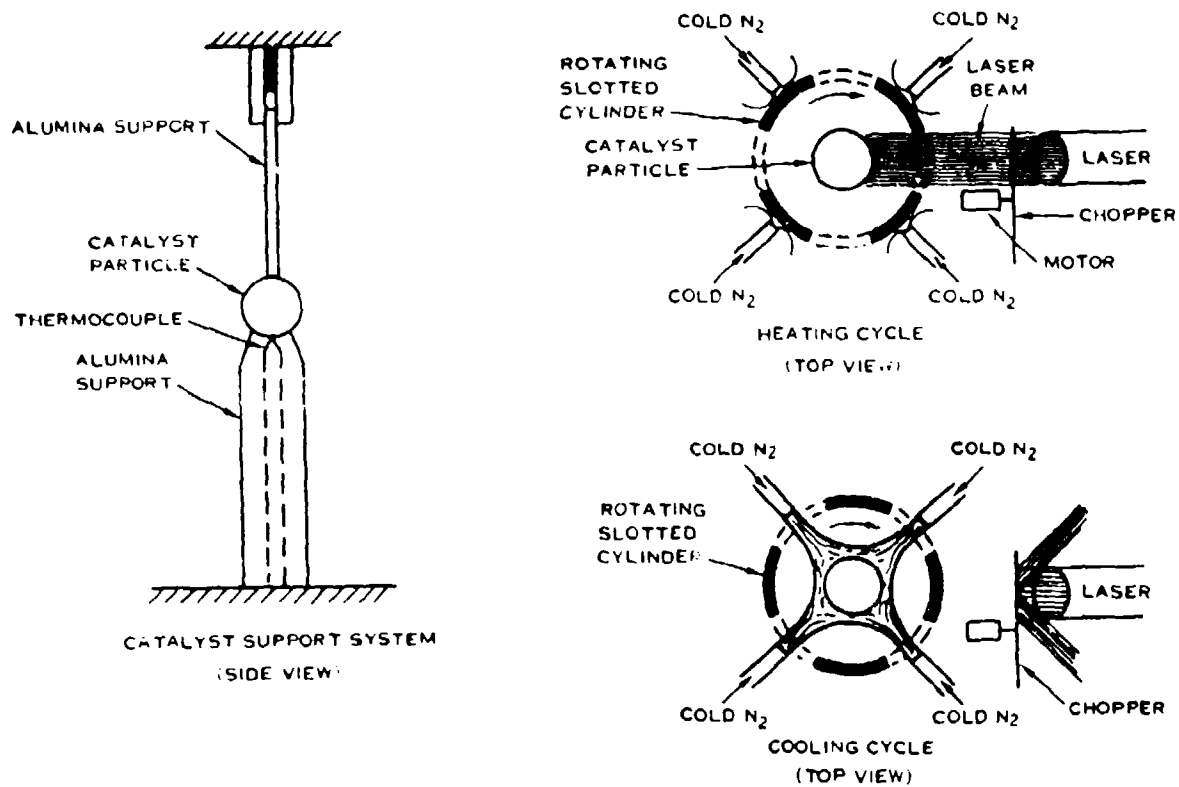
COOLING CYCLE
(TOP VIEW)

FIGURE 7

Particles were attached with contact cement to a ceramic rod and lowered against a small chromel-alumel thermocouple. With cooling gas flowing and shutter rotating, the laser beam was directed at the particle. The heating/cooling cycle was continued for three minutes, with pyrometer readings taken at one minute intervals. Approximately 1500 cycles were applied to each particle; in selected cases this was extended to approximately 10000 cycles.

Four batches of Shell 405 catalyst were used in this series: 14-18 mesh, Lot 12-MEM, and 20-30 mesh, Lot 10-MEM, both as-received, and two samples of similar sizes supplied by AFRPL. Complete details of the AFRPL engine tests are given in Ref. 5. All four batches were also used in liquid immersion tests.

Results and Discussion

The results of thermal shock tests are summarized in Table 7. As indicated in the summary, as-received particles of both 14-18 and 20-30 mesh sizes were essentially unaffected by thermal shock. Neither heating nor cooling caused breakage, except for one 14-18 mesh particle which broke upon immersion. All samples were recovered. Particle substrate integrity did not appear to be greatly affected; none of these particles broke during manipulation with tweezers after the tests.

Samples furnished by AFRPL exhibited noticeably different behavior. During part of the test series of L > 25 particles (nominal 14-18 mesh from a lower bed) some particles broke during heating and a significant number broke on quenching. Overall, the L > 25 samples showed increasing tendency to break during quench as the particle temperature was increased. These results are shown graphically in Fig. 8. In addition, some particles which did not break in the thermal shock tests were very fragile in the normal handling, i.e., removal from the water with tweezers and mounting on paper with clear tape.

The smaller particles from an upper bed (U > 30) showed essentially the same behavior, although only one sample broke upon heating. The trend to greater breakage at higher temperature was similar, as shown in Fig. 8. The summary results of all tests are also shown in Fig. 8; the fit to a single line is approximately the same for all data, indicating the particles are much the same. The greater fragility of the previously fired samples would appear to be caused by a lower substrate strength following the extensive engine firing; this may reflect the application of many thermal stresses during startup and run cycles.

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TABLE 7

PARTICLE BREAKUP IN THERMAL SHOCK TESTS

Sample	Temperature, F	No. Samples	Breakage During Heating	Breakage Upon Cooling
14-18 mesh,	< 1000	35	0	0
Lot 12-MEM	1000	11	0	0
as received	1200	11	0	1
	1400	14	0	0
	1600	11	0	0
	1800	5	0	0
20-30 mesh,	< 1000	30	0	0
Lot 10-MEM	1000	10	0	0
as received	1200	10	0	0
	1400	10	0	0
	1600	10	0	0
	1800	5	0	0
	2000	2	0	0
14-18 mesh,	< 1000	2	0	0
L > 25	1000	21	?	0
AFRPL-supplied	1200	17	1	0
sample (Ref. 2)	1400	20	3	2
	1600	22	2	4
	1800	22	2	5
	2000	10	0	4
20-30 mesh,	< 1000	6	0	0
U > 30	1000	16	0	1
AFRPL-supplied	1200	20	0	1
sample (Ref. 2)	1400	10	0	2
	1600	20	0	6
	1800	20	1	5
	2000	20	0	8

PARTICLE BREAKAGE BY THERMAL SHOCK:
EFFECT OF PARTICLE TEMPERATURE

ENGINE–FIRED PARTICLES

(HISTORY GIVEN IN REF. 1)

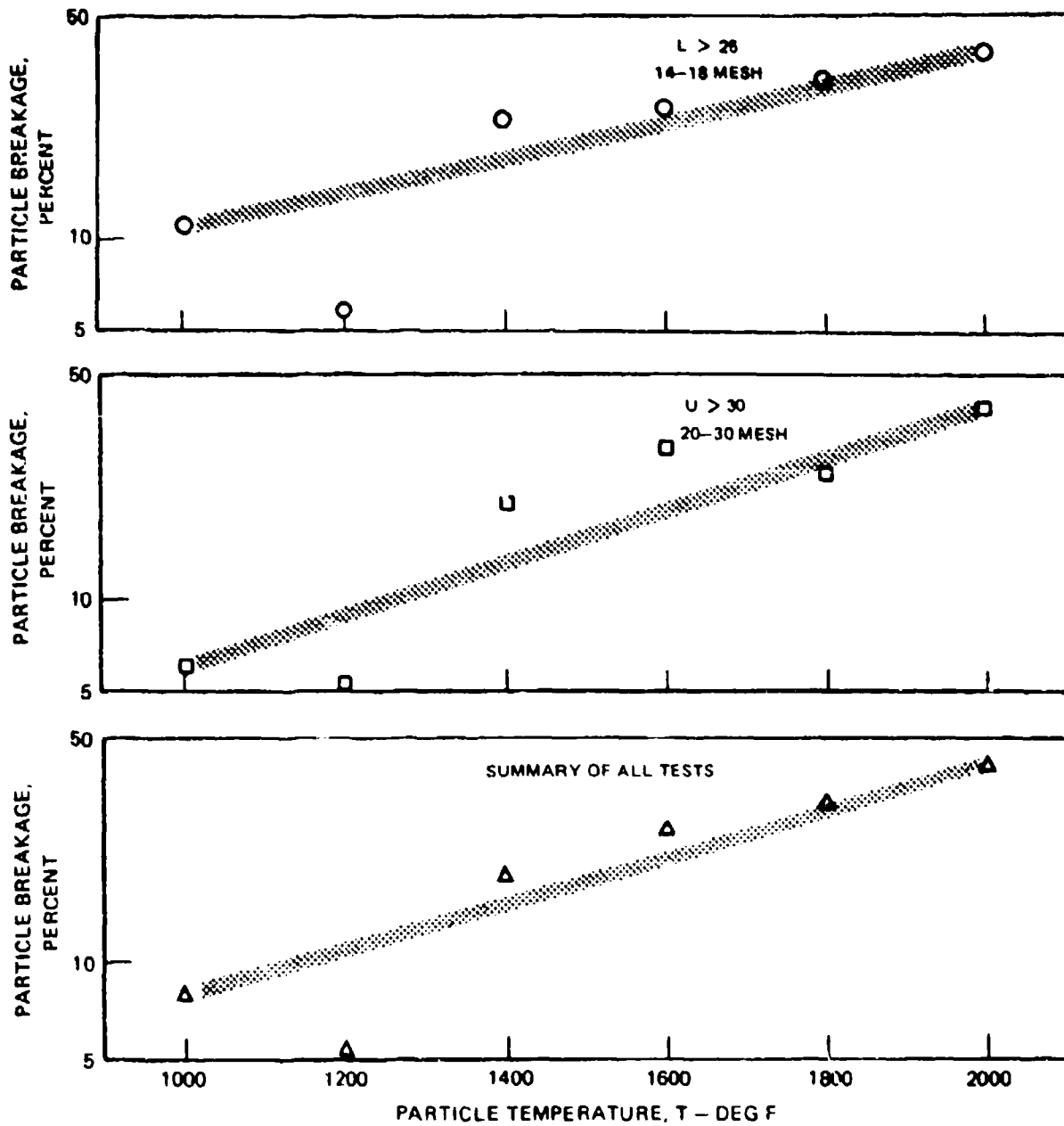FIGURE 8

Although the object of this series of tests was to induce thermal stress by rapid cooling from high temperature, breakage of some L > 25 particles upon heating indicated establishment of large thermal stress during this phase in a limited number of tests. One possible cause of the few heatup breaks found may be a combination of optical conditions leading to an unusually small and hot beam. Laser tube cleaning and various optical adjustments were frequently required, and all of the heatup breakage occurred between two adjustments. The possible rapid heating rate may not have been fully indicated by the thermocouple, although the net heating time appeared to be essentially the same. In a separate series of tests, the laser power was varied to determine whether heating rate might influence breakage. For most particles, the time to attain final temperature was approximately 2-3 sec. This corresponds to temperature increases of approximately 500 to 1000 deg F/sec. In specific tests, the heating time was extended to 8 to 10 sec or shortened to the minimum possible of just under 2 sec. No significant change in behavior was found, and no further heatup breakage occurred.

Breakage by thermal stresses induced by thermal cycling did not occur in any of the particles tested. The most noticeable feature of the experiments is a small (less than 100 F) drop in radiated temperature over the course of each experiment. Irradiated particles, upon visual examination, appear to be less porous, slightly glazed and metallic on the exposed surface. Temperature drop may be due to surface sintering which reduces the energy adsorbed.

Illustration of the surface changes induced by the long thermal cycling is given in Fig. 9. As-received and irradiated samples of two batches are shown. In the case of a particle from batch 12-MEM, the irradiated sample shows a number of large cracks and apparent sintering of the surface. In the case of the sample of batch 6-LEM, the structure changes are accompanied by a white deposit typical of most irradiated particles.

Analysis of the surface of the two laser-heated particles on Fig. 9 using x-ray techniques in the scanning electron microscope indicates that the surface loading of catalystic metal (iridium) has decreased substantially on exposed surfaces. This is shown in Fig. 10. This reduction in iridium loading would lead to greatly decreased activity of this area of the catalyst. (In Fig. 10, the trace superimposed on the particles is proportional to iridium concentration. Occasional reductions in the trace represent changes in beam focus caused by particle irregularities.)

PHOTOGRAPHS OF SHELL 405 CATALYST PARTICLES
BEFORE AND AFTER THERMAL CYCLING

MAGNIFICATION 25X

BATCH	BEFORE	AFTER
6 LEM 14-18 MESH		
12-MEM 14-18 MESH		

FIGURE 9

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SCANNING ELECTRON MICROSCOPE ANALYSIS OF SHELL 405 CATALYST PARTICLES
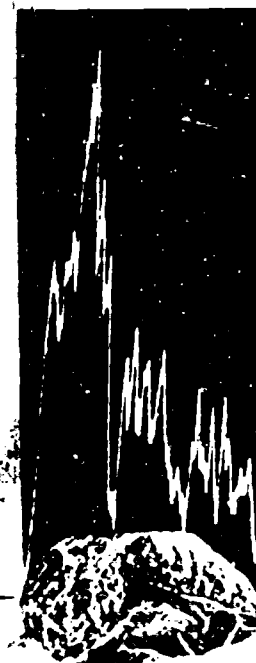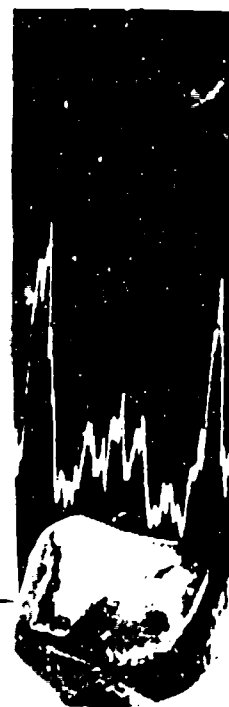## BEFORE AND AFTER THERMAL CYCLING

BATCH

BEFORE

AFTER

6-LEM
14-18 MESH

12-MEM
14-18 MESH

IRIDIUM CONCENTRATION

IRIDIUM CONCENTRATION

IV. CONCLUSIONS

1. The importance of wetting as a mechanism of catalyst particle breakup has been confirmed in this investigation. Important relationships between liquid temperature, catalyst reactivity and catalyst wetting and breakup have been determined.

2. The strongest influence on wetting is the temperature of liquid hydrazine in which particles are immersed. For a given catalyst particle reactivity increases markedly with temperature, since the liquid hydrazine vapor pressure is very sensitive to temperature and it is the vapor which decomposes on the catalyst surface.

3. Immersion of particle at fixed temperature may result in either wetted or nonwetted state. Heating of the system produces spontaneous change to nonwetted conditions at a characteristic transition temperature.

4. Although an average transition temperature exists for each batch of catalyst, the transition temperature is not precisely the same for all particles, indicating that particles of varied characteristics are found in each sample.

5. Particles which were exposed at low initial temperatures were found to be more susceptible to breakup on reactor heating. This suggests that wetting is temperature dependent with respect both to penetration depth and area.

6. The physical size of particles was found to be important. Both transition temperature and breakage were found to increase with decreasing particle size.

7. Tests were conducted to determine the effect of repetitive wetting on breakup, in order to examine whether particles breaking on initial exposure represent inherently weaker substrates. Very low breakage was found upon successive immersion. However, since reuse of particles alters the characteristics from the initial as-received state, the results are inconclusive.

8. The magnitude of flow velocity does not affect breakup of individual particles. However, in a packed bed reactor liquid velocity determines the depth of penetration into the bed and the number of particles which may potentially be wet.

9. A simplified thin slab model of a porous particle was used to make an assessment of nonuniform wetting on stressing of particle structure. Temperature rises of only a few degrees were calculated for liquid hydrazine temperatures of interest. This would indicate that enhancement of pressure stress by thermal stress induced by nonuniform wetting is small.

10. Engine-fired samples showed greater breakage than as-received catalyst. However, samples tested were from two locations of a single test engine, and the results must be considered to depend upon the history of that particular engine.

11. Low-temperature heating produced a surprisingly large and favorable effect on breakage. For heating conditions under which neither pore nor structural changes would be expected, reduction in breakage without change in activity was found.

12. Treatment with ammonia gas before liquid immersion caused a decrease in activity and increase in breakage.

13. Treatment with hydrogen gas at 50 psig produced the unexpected result of substantial decrease in breakage with little change in activity. This suggests that changes in activity and breakup are not necessarily coupled, and that potentially favorable effects in one characteristic may be obtained without change in another.

14. Inorganic contaminants (iron and zinc) and a manufacturing impurity (aniline) both caused a decrease in activity and increase in breakup.

15. As-received particles were unaffected by thermal shock. Engine-fired particles exhibited moderate breakage or were made more fragile by thermal shock.

16. Thermal cycling was found to be ineffective in breaking particles. Tests were conducted for a typical duty cycle (60 msec heating/60 msec cooling) with particle temperatures reaching 1900 F. For exposure times up to 20 minutes (approximately 10,000 cycles), no breakup was detected.

V. RECOMMENDATIONS

Breakup of catalyst particles caused by wetting and internal pressure buildup has been shown in these experiments to be of great importance. Wetting is controlled by a combination of two factors: the temperature of hydrazine to which particles are exposed, and the intrinsic activity of the particles.

The liquid temperature determines the hydrazine vapor pressure and decomposition; for a particular particle a higher temperature leads to greater rate of reaction and lower probability of wetting. Within an ensemble of particles at a fixed hydrazine temperature, those which are intrinsically most reactive would be least likely to wet. These experiments have shown that individual particle reactivity varies over a considerable range as evidenced by the distribution of transition temperatures for each batch.

To elucidate further the effect of intrinsic activity on wetting and subsequent breakup, it is important to evaluate the reactivity of individual catalyst particles. For this reason, a program is suggested to measure the activity of individual catalyst particles using kinetic as well as equilibrium methods and to correlate the results of these measurements with a measure of "wettability" in the hydrazine system. While the objective of this work is to obtain a clearer understanding of the relationship between activity and breakup, it may ultimately provide a method for screening of an ensemble of catalyst particles with respect to reactivity in hydrazine.

Breakup is also affected by the physical characteristics of catalyst particles. The pore size and pore size distributions play an important role in determining the degree of wetting, the magnitude of internal pressure rise, and the differential pressure stresses across pore walls. Changes in particle characteristics can be induced by heating or gas adsorption. In the experiments reported here, it has been indicated that particle heating and hydrogen preconditioning can, under certain conditions, lead to reduction in breakup without change in catalyst activity. These imply changes in pore size distribution, surface wettability, or particle strength characteristics. Work is required to measure the effects of catalyst preconditioning on both catalyst activity and physical characteristics and to correlate these effects with the results of wetting and breakup tests.

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